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AN ANALYTICAL METHOD FOR DETERMINING TRACE LEVELS OF SULFUR HEXAFLUORIDE, BROMOTRIFLUOROMETHANE AND DICHLORODIFLUOROMETHANE IN MINE AIR SAMPLES

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AN ANALYTICAL METHOD FOR DETERMINING TRACE LEVELS OF SULFUR HEXAFLUORIDE, BROMOTRIFLUOROMETHANE AND DICHLORODIFLUOROMETHANE IN MINE AIR SAMPLES

by

D.J. Kennedy*

ABSTRACT

Traditionally sulfur hexafluoride has been used as a tracer gas for analyzing mine ventilation networks. Many mine ventilation problems could be better evaluated using two or more tracer gases simultaneously. This report describes the analytical method and equipment used to measure trace levels of sulfur hexafluoride, bromotrifluoromethane and dichlorodifluoromethane in mine air samples.

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MÉTHODE ANALYTIQUE POUR DÉTERMINER LES CONCENTRATIONS DE TRACES D'HEXAFLUORURE DE SOUFRE, DE BROMOTRIFLUOROMÉTHANE ET DE DICHLORODIFLUOROMÉTHANE DANS LES ÉCHANTILLONS D'AIR PROVENANT DES MINES

par

D.J. Kennedy*

RÉSUMÉ

Traditionnellement, l'hexafluorure de soufre a été utilisée pour analyser les réseaux de ventilation des mines. Plusieurs problèmes inhérents à la ventilation des mines pourraient être évalués de façon plus précise si on utilisait simultanément deux gaz traces ou plus. L'auteur présente la méthode scientifique et l'appareillage qui ont été utilisés pour mesurer les concentrations de traces d'hexafluorure de soufre, de bromotrifluorométhane et de dichlorodifluorométhane dans les échantillons d'air recueillis dans les mines.

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INTRODUCTION

The Cape Breton Coal Research Laboratory uses sulfur hexafluoride as a tracer gas for analyzing mine ventilation systems. During the course of our investigations, the advantages of using two or more different tracer gases to evaluate mine ventilation problems became evident. This report describes the analytical method we developed to measure parts per billion levels of sulfur hexafluoride, bromotrifluoromethane and dichlorodifluoromethane in mine air samples.

DEVELOPMENT OF THE ANALYTICAL METHOD

Trace levels of sulfur hexafluoride in air have traditionally been analyzed by gas chromatography utilizing an electron capture detector. High purity nitrogen or 5% methane in argon is normally used as the carrier gas. The analytical column, a short length of tubing packed with molecular sieve 5A, separates sulfur hexafluoride from other gases present in the sample.

Heggen and Oehme (1) describe a column for analyzing sulfur hexafluoride and bromotrifluoromethane in air samples. They use molecular sieve 5A as the adsorbent material, however the length of their column is about five times that needed for sulfur hexafluoride analysis. This length is necessary to separate bromotrifluoromethane from oxygen. When the column is operated at 40°C, an analysis time of 3 min/sample is reported.

Two problems with this method are: 1) analysis time is increased waiting for the oxygen peak to elute after the two tracer gases and 2) interferences caused by other gases, especially Freons, can greatly increase analysis time or prevent analysis altogether.

These problems may be overcome by backflushing the oxygen and other gases to vent after the two tracer gases have eluted from the column. This technique also ensures long-term stability of the analytical system and should be used for any tracer gas analysis.

SULFUR HEXAFLUORIDE AND BROMOTRIFLUOROMETHANE ANALYSIS

Figure 1 shows a diagram of a Valco 10-port multi-functional gas sampling valve. This valve can be used for both gas sampling and back-flushing (2).

Our system uses this valve in a Perkin-Elmer Sigma 2000 gas chromatograph equipped with an electron capture detector.

Column 1 is a 3.2 mm x 457 mm (1/8" x 18") stainless steel column packed with molecular sieve 5A (80/100 mesh). Column 2 is a 3.2 mm x 1829 mm (1/8" x 72") stainless steel column also packed with molecular sieve 5A (80/100 mesh).

The following instrument conditions are used:

Sample loop	-	50 l
Valve temperature	-	40°C
Oven temperature	-	50°C
Detector temperature	-	100°C
Carrier flow	-	20 ml/min

The valve operation is microprocessor controlled with backflushing occurring 0.43 minutes after sample injection. This allows an analysis time of 2 min/sample. Figure 2 shows a chromatograph of a gas mixture containing 101 ppb sulfur hexafluoride, 205 ppb bromotrifluoromethane and 181 ppb dichlorodifluoromethane in air.

The retention time of sulfur hexafluoride is 0.70 minutes and that of bromotrifluoromethane is 1.37 minutes. A small portion of the oxygen peak enters column 2 before column 1 is backflushed. Dichlorodifluoromethane and other gases are backflushed to vent.

This system may also be used for sulfur hexafluoride analysis alone. If the valve is switched 0.23 minutes after sample injection, bromotrifluoromethane is also backflushed to vent. An analysis time of 1 sample/min is possible.

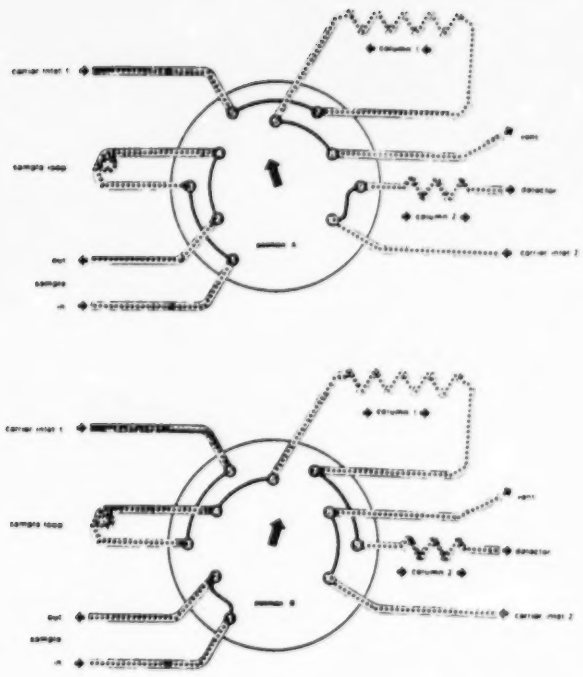

Figure 1 - Diagram of a Valco 10-port multi-functional gas sampling valve

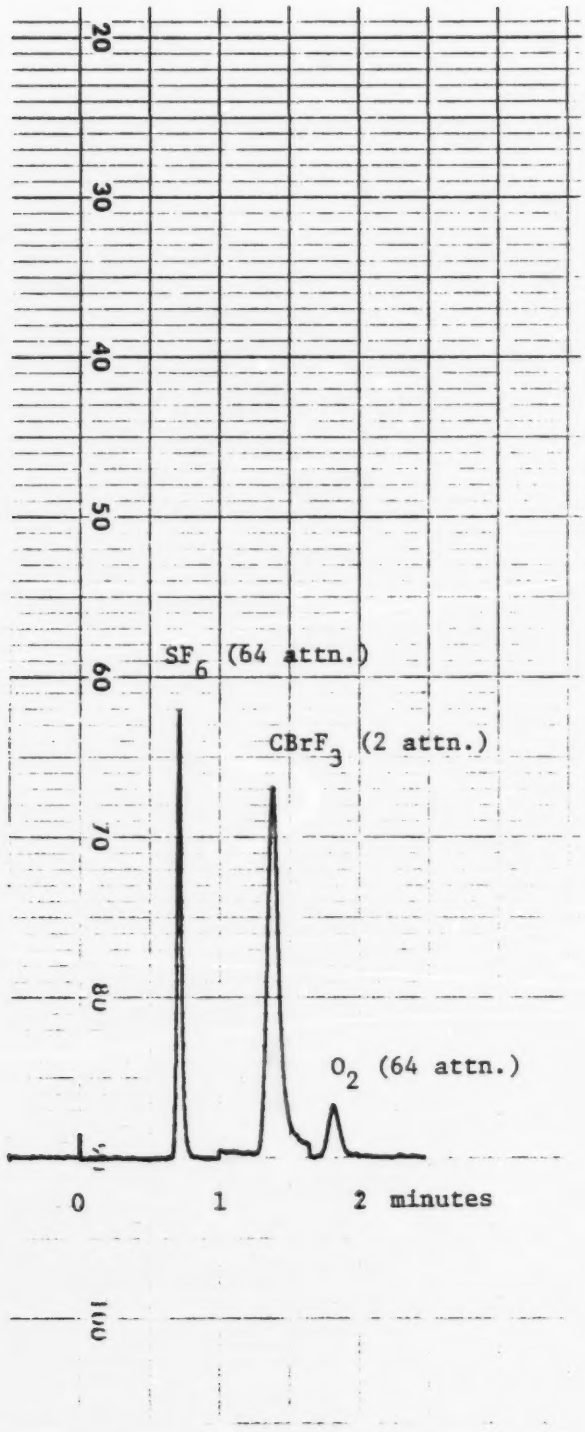

Figure 2 - Chromatograph of a gas mixture containing 101 ppb sulfur hexafluoride, 205 ppb bromotrifluoromethane and 181 ppb dichlorodifluoromethane in air

DICHLORODIFLUOROMETHANE ANALYSIS

The electron capture detector responds differently to each of the tracer gases. If the response of dichlorodifluoromethane is set at 1, then the response of bromotrifluoromethane would be 4 and the response of sulfur hexafluoride would be 120.

A separate gas sampling/switching valve with a 0.5 cc sample loop is used for dichlorodifluoromethane analysis. Figure 3 shows a chromatograph of the gas mixture containing 101 ppb sulfur hexafluoride, 205 ppb bromotrifluoromethane and 181 ppb dichlorodifluoromethane in air on a Porapak Type P column. The column is 3.2 mm x 610 mm (1/8" x 24") stainless steel packed with acetone washed Porapak Type P (80/100 mesh).

The following instrument conditions are used:

Sample Loop	-	0.5 cc
Valve Temperature	-	50°C
Oven Temperature	-	50°C
Detector Temperature	-	100°C
Carrier Flow Rate	-	19 ml/min

The retention time of bromotrifluoromethane is 0.74 minutes and that of dichlorodifluoromethane is 1.86 minutes.

Water vapor elutes from a Porapak Type P column just before dichlorodifluoromethane. To prevent the water peak from interfering, the gas sample must be dried before it is injected into the Porapak Type P column. A 6.4 mm x 152 mm (1/4" x 6") length of teflon tubing filled with Drierite may be used for this purpose.

INSTRUMENT PLUMBING FOR THREE TRACER GASES

The instrument plumbing consists of three Valco valves. Valves A and B are 10-port multi-functional valves as shown in Figure 1. Valve A is configured with MS5A columns as described for sulfur hexafluoride and bromotrifluoromethane analysis. Valve B is configured for dibromodichloromethane analysis as follows:

column 1 - 3.2 mm x 457 mm (1/8" x 18") stainless steel
packed with molecular sieve 5A (80/100 mesh)

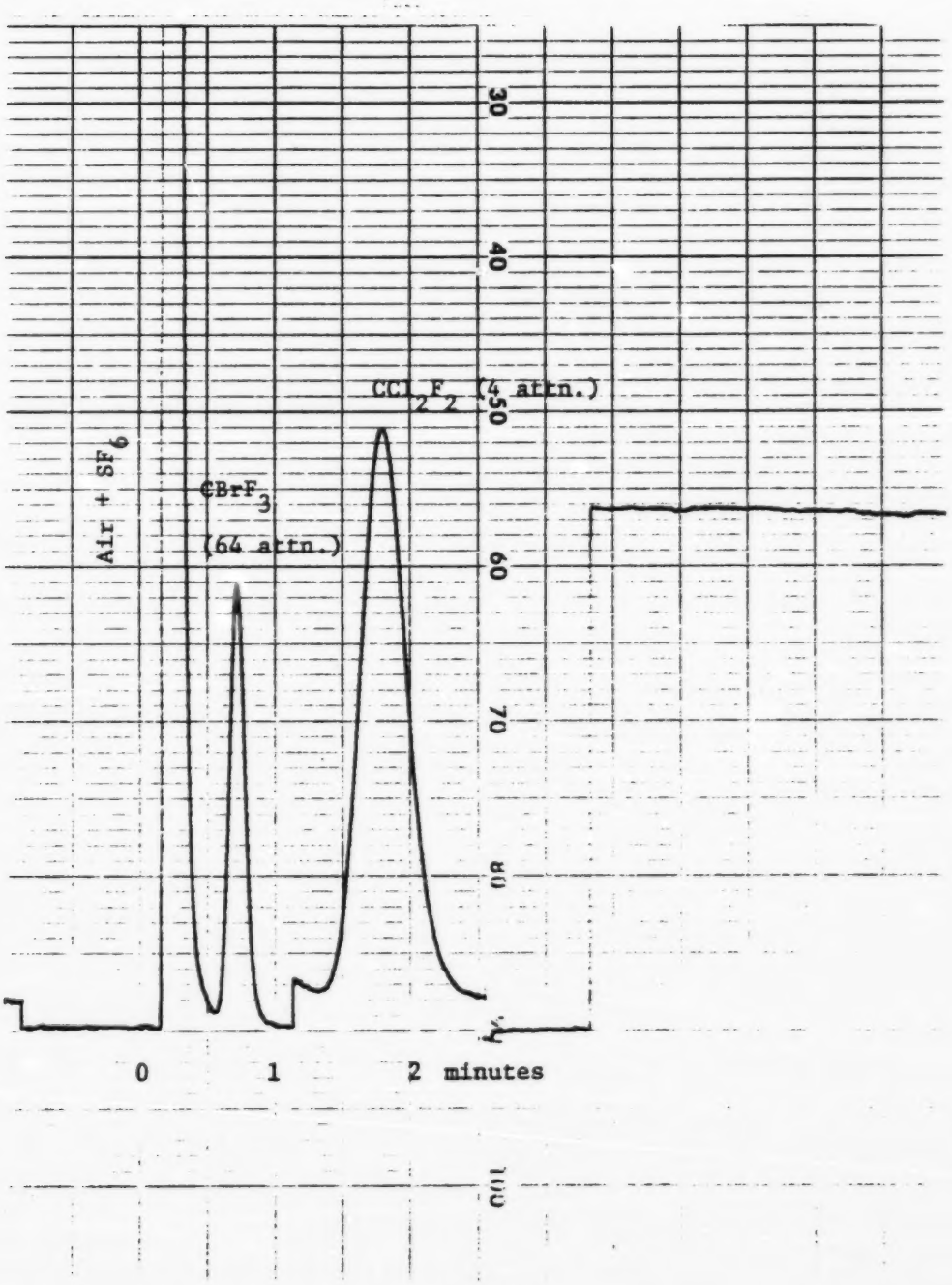

Figure 3 - Chromatograph of a gas mixture containing 101 ppb sulfur hexafluoride, 205 ppb bromotrifluoromethane and 181 ppb dichlorodifluoromethane in air on a Porapak column

column 2 - 3.2 mm x 610 mm (1/8" x 24") stainless steel packed with acetone washed Porapak Type P (80/100 mesh)

sample loop - 0.5 cc

In low concentrations, dichlorodifluoromethane elutes from a molecular sieve 5A column just after oxygen. Valve B is switched after dibromodichloromethane passes onto the Porapak Type P column thus backflushing other gases to vent. The use of a molecular sieve column in series with the Porapak Type P column also eliminates the need for a drier. Water vapor is adsorbed by the molecular sieve, however this must be removed by reconditioning the column when it will no longer separate components of interest.

Valve C is a 4-port switching valve located between the electron capture detector and the other two valves. This allows the effulent from column 2 of valve A to be directed to the detector while the effulent from column 2 of valve B is directed to vent. Switching valve C reverses this connecting column 2, valve B to the detector while venting column 2, valve A.

Figure 4 shows a chromatograph of the gas mixture containing 101 ppb sulfur hexafluoride, 205 ppb bromotrifluoromethane and 181 ppb dichlorodifluoromethane in air using this method.

Instrument conditions are as follows:

Valve A (50 µl sample) - 40°C
Valve B (0.5 cc sample) - 50°C
Oven Temperature - 50°C
Detector Temperature - 100°C
Carrier Flow Valve A - 20 ml/min
Carrier Flow Valve B - 16 ml/min
0.00 min - Attenuation: X 32
0.02 min - Valve A inject
0.02 min - Valve B inject
0.45 min - Valve A backflush
0.80 min - Valve B backflush
0.96 min - Attenuation: X 1
1.75 min - Valve C switched
1.75 min - Attenuation: X 4
3.50 min - Valve C switched

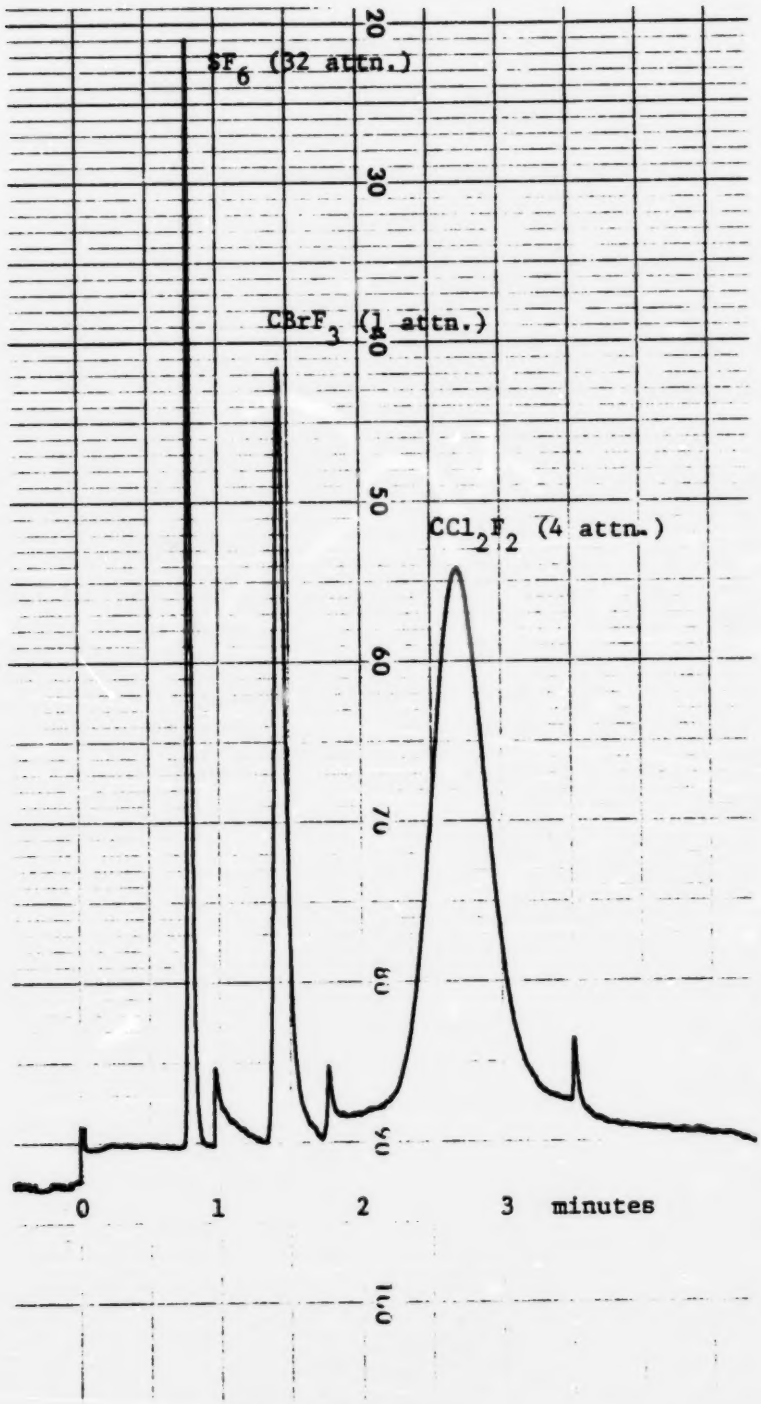

Figure 4 - Chromatograph of a gas mixture containing 101 ppb sulfur hexafluoride, 205 ppb bromotrifluoromethane and 181 ppb dichlorodifluoromethane

CONCLUSIONS

The length of the Porapak Type P column should be increased by 25% allowing the carrier flow through this column to be increased to match that of the molecular sieve column on valve A. The baseline upset occurring when valve C is switched would then be minimized.

If a large enough sample is available for use with a drier, then the author would suggest removing valve C from the system. Valve A could be optimized for sulfur hexafluoride analysis using molecular sieve 5A columns with an analysis time of 30 sec/sample. Valve B could be configured with two Porapak Type P columns for bromotrifluoromethane and dichlorodifluoromethane analysis. The drier would only be needed for dichlorodifluoromethane analysis.

The need for proper cleaning procedures cannot be overemphasized. These are described in an earlier paper (3). The Porapak Type P column packing material should be thoroughly washed with high purity acetone and the columns made with it well conditioned. The Porapak Type P columns prepared by the author were conditioned for three days at 150°C. These columns gave as low a background signal on the electron capture detector as a well conditioned molecular sieve column.

REFERENCES

1. Heggen, R. and Oehme, M. "Columns for simultaneous gas chromatographic determination of ppt levels of the atmospheric tracers sulphur hexafluoride and bromotrifluoromethane in ambient air samples"; Journal of Chromatography; 243; pp. 168-172; 1982.
2. "Bulletin on 10-port multi-functional gas sampling valves"; Valco Instruments Co. Inc., Houston, Texas.
3. Kennedy, D.J. "A rapid sequential tracer gas analyzer suitable for use in the underground environment"; CANMET Division Report ERP/CRL 86-70(TR); June 1986.